

One and two-component hard-core plasmas

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A field theory is presented for particles which interact via Coulomb and hard-core potentials. We apply the method to the one-component plasma (OCP) with hard cores, consisting of identical particles of fixed charge and diameter in a neutralizing background, and the symmetric two-component plasma (TCP) with hard cores, consisting of equal numbers of positively and negatively charged particles of identical size. We obtain exactly the first few coefficients of a systematic low-density expansion of the free energy for both models. The OCP coefficients go over to the classical Abe result in the high-charge (or small hard-core diameter) limit. The TCP, on the other hand, exhibits diverging coefficients in the high-charge limit, which is due to the formation of strongly bound ion-pairs.

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I. INTRODUCTION

The equation of state of a one-component plasma (OCP), i.e. of a system consisting of point-like charged particles, is of central importance for plasma theory [1]. It is commonly assumed that the OCP follows from the two-component plasma (TCP), consisting of a globally neutral mixture of positive and negative point particles, if one charge species is of lesser charge and forms a neutralizing background. Much interest in the plasma community has been focused on the limit of high plasma density (or large plasma parameter), which defines the limit when the electrostatic interaction at average separation between two particles is much larger than thermal energy [2]. This situation is, for example, realized in white dwarfs and the interior of large planets (such as Jupiter). Our interest in plasmas comes mainly from the close analogy with colloidal and electrolyte solutions, which also consist of charged particles. Very often in colloidal systems, the concentration of charged species is rather low, such that a low-density expansion becomes meaningful. Also, in addition to Coulombic interactions, the excluded-volume interaction becomes important in colloidal and electrolyte systems, and therefore has to be included [3]. The OCP without hard core interactions has been studied by a variety of methods [1]. The first few terms in a low-density expansion of the free energy have been obtained by an explicit resummation of the Mayer expansion [4]. The OCP with hard cores has in the past been studied extensively with numerical and integral-equation methods [5]. For the TCP, the leading term in the free energy has been calculated by Debye and Hückel in their classical paper [6]. The formal foundation for the rigorous thermodynamic treatment of a TCP including a hard-core interaction has been given by Mayer [7] and Edwards [8], but to our knowledge, no systematic calculation of the low density expansion of the free energy has been performed.

In this article, we present a novel field-theoretic method which can be used to systematically calculate free energies and other quantities of interest for systems of charged hard-core particles in powers of particle densities. We apply this method both to the OCP and TCP in the presence of finite hard-core radii. In the limit of vanishing particle charges, we recover the virial expansion of a hard core gas for both the OCP and TCP. In the limit of vanishing hard-core radius, we recover the classical Abe result for the OCP [4]. The expansion coefficients of the TCP diverges in the limit of vanishing hard-core radius, due to the proliferation of bound particle pairs. Much interest has been focused on the critical behavior of the TCP with hard core interactions (the so-called restricted primitive model, RPM) [9–13]. Our results demonstrate that the critical point of the RPM is not accessible by a low-density expansion.

In the next two sections we present our methods and calculations for the TCP and OCP with hard cores, respectively. Our main results consist of the density expansion coefficients of the free energy, which are obtained in closed form for the full range of coupling constants. The final section is devoted to a brief discussion of our results.

II. TWO-COMPONENT PLASMA

We consider a gas of N_+ positive charges and N_- negative charges, interacting with Coulomb interactions $v(\mathbf{r}) = \ell_B/r$ and an additional short-ranged potential $w(\mathbf{r})$ which we assume to be a hard-core interaction of range a . The

Bjerrum length $\ell_B = q^2/4\pi\epsilon k_B T$ measures the distance at which the interaction between two charged particles equals the thermal energy. The canonical partition function of the system reads

$$Z_{N_+, N_-} = \frac{1}{N_+! N_-!} \prod_{i=1}^{N_+} \left[\int d\mathbf{r}_i^+ \right] \prod_{i=1}^{N_-} \left[\int d\mathbf{r}_i^- \right] \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' [\rho(\mathbf{r}) w(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') + \rho_c(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \rho_c(\mathbf{r}')] \right\} e^{(N_+ + N_-)[w(0) + v(0)]/2} \quad (1)$$

where

$$\rho(\mathbf{r}) = \sum_{i=1}^{N_+} \delta(\mathbf{r} - \mathbf{r}_i^+) + \sum_{i=1}^{N_-} \delta(\mathbf{r} - \mathbf{r}_i^-)$$

denotes the particle density and

$$\rho_c(\mathbf{r}) = \sum_{i=1}^{N_+} \delta(\mathbf{r} - \mathbf{r}_i^+) - \sum_{i=1}^{N_-} \delta(\mathbf{r} - \mathbf{r}_i^-)$$

is the charge density. The infinite particle self-energies $v(0)$ and $w(0)$ are subtracted. We perform a double Stratanovitch-Hubbard transform and get

$$Z_{N_+, N_-} = \int \frac{\mathcal{D}\phi}{Z_v} \int \frac{\mathcal{D}\psi}{Z_w} \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' [\psi(\mathbf{r}) w^{-1}(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}') + \phi(\mathbf{r}) v^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}')] \right\} \frac{1}{N_+!} \left[\int d\mathbf{r} e^{-i\psi(\mathbf{r}) - i\phi(\mathbf{r}) + w(0)/2 + v(0)/2} \right]^{N_+} \frac{1}{N_-!} \left[\int d\mathbf{r} e^{-i\psi(\mathbf{r}) + i\phi(\mathbf{r}) + w(0)/2 + v(0)/2} \right]^{N_-} \quad (2)$$

where Z_v and Z_w denote the square root of the determinants of the Coulomb and hard-core operators, $Z_v \sim \sqrt{\det v}$ and $Z_w \sim \sqrt{\det w}$, respectively. Assuming that the fugacities of the positive and negative ions are the same, the grand-canonical partition function is defined by

$$Z_\lambda = \sum_{N_+, N_-} \lambda^{N_+ + N_-} Z_{N_+, N_-} \quad (3)$$

and reads

$$Z_\lambda = \int \frac{\mathcal{D}\phi}{Z_v} \int \frac{\mathcal{D}\psi}{Z_w} \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' [\psi(\mathbf{r}) w^{-1}(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}') + \phi(\mathbf{r}) v^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}')] \right. \\ \left. + 2\lambda \int d\mathbf{r} h(\mathbf{r}) e^{v(0)/2} \cos[\phi(\mathbf{r})] \right\} \quad (4)$$

where we used the definition

$$h(\mathbf{r}) \equiv e^{-i\psi(\mathbf{r}) + w(0)/2}. \quad (5)$$

We next introduce the Debye-Hückel propagator, whose inverse is given by the ordinary screened Coulomb potential $v_{\text{DH}}(\mathbf{r}) = \ell_B e^{-\kappa r}/r$ with $\kappa^2 = 8\pi\ell_B \lambda$. The partition function can be written as

$$Z_\lambda = e^{2\lambda V + \lambda V v(0)} \frac{Z_{\text{DH}}}{Z_v} \left\langle e^{2\lambda \int d\mathbf{r} Q(\mathbf{r})} \right\rangle \quad (6)$$

where

$$Q(\mathbf{r}) \equiv h(\mathbf{r}) e^{v(0)/2} \cos[\phi(\mathbf{r})] - 1 - v(0)/2 + \phi^2(\mathbf{r})/2 \quad (7)$$

and the average brackets denote averages with respect to the DH propagator and the hard-core propagator. The determinant of the Debye-Hückel interaction is denoted as $Z_{\text{DH}} \sim \sqrt{\det v_{\text{DH}}}$ and will be explicitly calculated below. Defining the effective interaction Q in this fashion allows us to perform a systematic low-density expansion, since all

higher cumulant expectation values of Q are finite even if the fugacity inside the Debye-Hückel propagator is set to zero. The logarithm of the partition function is given by a cumulant expansion in powers of Q ,

$$\frac{\ln Z_\lambda}{V} = 2\lambda + \lambda v(0) + V^{-1} \ln \left[\frac{Z_{\text{DH}}}{Z_v} \right] + 2\lambda Z_1 + 2\lambda^2 Z_2 + \dots \quad (8)$$

where

$$Z_1 = V^{-1} \int d\mathbf{r} \langle Q(\mathbf{r}) \rangle, \quad (9)$$

$$Z_2 = V^{-1} \int d\mathbf{r}_1 d\mathbf{r}_2 \langle Q(\mathbf{r}_1) Q(\mathbf{r}_2) \rangle - V^{-1} \left[\int d\mathbf{r} \langle Q(\mathbf{r}) \rangle \right]^2. \quad (10)$$

All expectation values appearing in these expressions can be calculated explicitly. We note that, neglecting the hard-core interaction, the cumulant terms Z_n correspond to giant cluster graphs considered by Abe [4]. Since the integrals with respect to the fluctuating ϕ and ψ fields decouple, we do not have to consider mixed expectation values. Up to second order in Q we only need the expectation values

$$\langle h(\mathbf{r}) \rangle = 1, \quad (11)$$

$$\langle h(\mathbf{r}_1) h(\mathbf{r}_2) \rangle = e^{-w(\mathbf{r}_1 - \mathbf{r}_2)}, \quad (12)$$

$$\langle \phi^2(\mathbf{r}) \rangle = v_{\text{DH}}(0), \quad (13)$$

$$\langle \phi^2(\mathbf{r}_1) \phi^2(\mathbf{r}_2) \rangle = 2v_{\text{DH}}^2(\mathbf{r}_1 - \mathbf{r}_2) + v_{\text{DH}}^2(0), \quad (14)$$

$$\langle \cos[\phi(\mathbf{r})] \rangle = e^{-v_{\text{DH}}(0)/2}, \quad (15)$$

$$\langle \cos[\phi(\mathbf{r}_1)] \cos[\phi(\mathbf{r}_2)] \rangle = e^{-v_{\text{DH}}(0)} \left(e^{-v_{\text{DH}}(\mathbf{r}_1 - \mathbf{r}_2)} + e^{v_{\text{DH}}(\mathbf{r}_1 - \mathbf{r}_2)} \right) / 2, \quad (16)$$

$$\langle \phi^2(\mathbf{r}_1) \cos[\phi(\mathbf{r}_2)] \rangle = e^{-v_{\text{DH}}(0)/2} (v_{\text{DH}}(0) - v_{\text{DH}}^2(\mathbf{r}_1 - \mathbf{r}_2)). \quad (17)$$

Introducing the difference between the Debye-Hückel and the bare Coulomb self energy, which is finite,

$$\Delta v_0 = v(0) - v_{\text{DH}}(0) = \ell_B \sqrt{8\pi\ell_B\lambda}, \quad (18)$$

the functions Z_1 and Z_2 can be explicitly written as

$$Z_1 = e^{\Delta v_0/2} - 1 - \Delta v_0/2, \quad (19)$$

$$Z_2 = \int d\mathbf{r} \left[\frac{1}{2} e^{\Delta v_0 - w(\mathbf{r})} \left(e^{-v_{\text{DH}}(\mathbf{r})} + e^{v_{\text{DH}}(\mathbf{r})} \right) - e^{\Delta v_0} + \frac{1}{2} v_{\text{DH}}^2(\mathbf{r}) \left(1 - 2e^{\Delta v_0/2} \right) \right]. \quad (20)$$

The DH contribution to the free energy in eq.(8) follows as

$$\lambda v(0) + V^{-1} \ln \left[\frac{Z_{\text{DH}}}{Z_v} \right] = -\frac{1}{2} \int \frac{d\mathbf{q}}{(2\pi)^3} \ln \left(1 + \frac{8\pi\ell_B\lambda}{q^2} \right) + \lambda \int \frac{d\mathbf{q}}{(2\pi)^3} \frac{4\pi\ell_B}{q^2} = \frac{(8\pi\ell_B\lambda)^{3/2}}{12\pi}. \quad (21)$$

Next we have to systematically carry out the back-Legendre transform to the canonical ensemble. To do this, we expand the grand-canonical potential in eq.(8) in fractional powers of the rescaled fugacity, $\tilde{\lambda} = a^3\lambda$,

$$\frac{a^3 \ln Z_\lambda}{V} = 2\tilde{\lambda} - b_{3/2}\tilde{\lambda}^{3/2} - b_2\tilde{\lambda}^2 - b_{5/2}\tilde{\lambda}^{5/2} - \dots \quad (22)$$

From the definition of the grand-canonical partition function, eq.(3), it follows that the rescaled concentration of ion pairs, $\tilde{c} = a^3(N_+ + N_-)/2V$, is given by

$$\tilde{c} = \frac{\lambda \partial a^3 \ln Z_\lambda / V}{2\partial \lambda}. \quad (23)$$

From eqs.(22) and (23) we obtain the fugacity as a function of the concentration

$$\tilde{\lambda} = \tilde{c} + \frac{3}{4}b_{3/2}\tilde{c}^{3/2} + \left(b_2 + \frac{27}{32}b_{3/2}^2\right)\tilde{c}^2 + \left(\frac{5}{4}b_{5/2} + \frac{21}{8}b_2b_{3/2} + \frac{567}{512}b_{3/2}^3\right)\tilde{c}^{5/2} + \dots \quad (24)$$

Inserting this into eq.(22), the rescaled free energy density follows as

$$\begin{aligned} a^3 f &= -\frac{a^3 \ln Z_\lambda}{V} + 2\tilde{c} \ln \tilde{\lambda} \\ &= 2\tilde{c} \ln \tilde{c} - 2\tilde{c} + d_{3/2}\tilde{c}^{3/2} + d_2\tilde{c}^2 + d_{5/2}\tilde{c}^{5/2} + \dots \end{aligned} \quad (25)$$

with the expansion coefficients given by

$$d_{3/2} = b_{3/2},$$

$$d_2 = b_2 + \frac{9}{16}b_{3/2}^2,$$

$$d_{5/2} = b_{5/2} + \frac{3}{2}b_2b_{3/2} + \frac{63}{128}b_{3/2}^3.$$

To carry out the expansion of the grand-canonical free energy shown in eq.(22), we also have to expand the functions Z_n in fractional powers of the fugacity,

$$Z_1 = \tilde{\lambda}z_1^{(1)} + \tilde{\lambda}^{3/2}z_1^{(3/2)} + \mathcal{O}(\tilde{\lambda}^2),$$

$$Z_2 = z_2^{(0)} + \tilde{\lambda}^{1/2}z_2^{(1)} + \mathcal{O}(\tilde{\lambda}).$$

Introducing the energy scale $\epsilon = \ell_B/a$ with a being the hard-core radius (or diameter of the spherical particles), we obtain from eq.(19)

$$z_1^{(1)} = \frac{\Delta v_0^2}{8\tilde{\lambda}} = \pi\epsilon^3 \quad (26)$$

$$z_1^{(3/2)} = \frac{\Delta v_0^3}{48\tilde{\lambda}^{3/2}} = \frac{(2\pi\epsilon^3)^{3/2}}{6} \quad (27)$$

From eq.(20) we obtain

$$z_2^{(0)} = \frac{\pi}{3} (2\epsilon^3 \text{Shi}[\epsilon] - e^\epsilon [2 + \epsilon + \epsilon^2] - e^{-\epsilon} [2 - \epsilon + \epsilon^2]) \quad (28)$$

where Shi is the hyperbolic sine-integral function defined by

$$\text{Shi}(z) = \int_0^z \frac{\sinh t}{t} dt \quad (29)$$

and

$$z_2^{(1/2)} = \frac{(2\pi\epsilon)^{3/2}}{3} \left(2\epsilon^3(\Gamma[\epsilon] + 2\gamma + \frac{1}{2}\ln[128\pi\epsilon^3\tilde{c}]) - 2e^{-\epsilon} [2 - \epsilon + \epsilon^2] - \frac{13}{6}\epsilon^3 \right) \quad (30)$$

The coefficient of the $\tilde{\lambda}^{3/2}$ term in eq.(22) follows from Eq.(21) as

$$b_{3/2} = -\frac{4}{3}\sqrt{2\pi}\epsilon^{3/2}, \quad (31)$$

the other coefficients are

$$b_2 = -2z_1^{(1)} - 2z_2^{(0)}, \quad (32)$$

$$b_{5/2} = -2z_1^{(3/2)} - 2z_2^{(1/2)}. \quad (33)$$

In the limit $\epsilon \rightarrow 0$, which corresponds to the pure hard-core case, we obtain $b_2 = +8\pi/3$, the well-known second-virial result. In the strong-coupling limit, $\epsilon \rightarrow \infty$, we obtain $b_2 = -4\pi e^\epsilon/\epsilon$. It is seen that the coefficient b_2 diverges exponentially as ϵ increases. We attribute this divergence to the formation of strongly bound ion pairs: the Boltzmann weight of a pair of oppositely charged ions which stick together is e^ϵ , which dominates the statistics for large values of ϵ . The next-leading coefficient $b_{5/2}$ is dominated by its logarithmic contribution and is given by $b_{5/2} = -2(2\pi)^{3/2}\epsilon^{9/2}\ln(\epsilon)$ both in the limit of small and large ϵ . In Fig.1 we plot the free energy coefficients d_2 and $d_{5/2}$ as a function of ϵ . For moderately large values of ϵ , it is seen that the coefficients increase exponentially and thus render the low-density expansion useless for large couplings and large densities. It follows that the critical point of the TCP, which is supposed to occur at coupling strengths of the order of $\epsilon \approx 15$ and a rescaled ion pair density of $\tilde{c} \approx 0.03$ [10], is inaccessible by such a low-density expansion.

As we will demonstrate in the following section, the OCP does not contain ion pairing and thus the expansion of the free energy in powers of the density is well-behaved even in the limit $\epsilon \rightarrow \infty$.

III. ONE-COMPONENT PLASMA

We now consider a gas of N identical charged particles, interacting with Coulomb and hard core potentials. We assume the existence of a uniform oppositely charged background, which exactly neutralizes the charges. At first, we will neglect this background charge, and identify and omit the (infinite) energy contribution of this background in our final free energy expression. The canonical partition function of the system reads:

$$Z_N = \frac{1}{N!} \prod_{i=1}^N \left[\int d\mathbf{r}_i \right] \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \rho(\mathbf{r}) [w(\mathbf{r} - \mathbf{r}') + v(\mathbf{r} - \mathbf{r}')] \rho(\mathbf{r}') + N[w(0) + v(0)]/2 \right\} \quad (34)$$

where $\rho(r) = \sum_{i=1}^N \delta(r - r_i)$ denotes the particle density. The infinite particle self-energies are subtracted. As we did for the TCP, we perform a double Stratanovitch-Hubbard transform and get

$$Z_N = \int \frac{\mathcal{D}\phi}{Z_v} \int \frac{\mathcal{D}\psi}{Z_w} \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' [\psi(\mathbf{r}) w^{-1}(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}') + \phi(\mathbf{r}) v^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}')] \right\} \frac{1}{N!} \left[\int d\mathbf{r} e^{-i\psi(\mathbf{r}) - i\phi(\mathbf{r}) + w(0)/2 + v(0)/2} \right]^N. \quad (35)$$

The grand canonical partition function is defined by

$$Z_\lambda = \sum_N \lambda^N Z_N \quad (36)$$

and reads

$$Z_\lambda = \int \frac{\mathcal{D}\phi}{Z_v} \int \frac{\mathcal{D}\psi}{Z_w} \exp \left\{ -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' [\psi(\mathbf{r}) w^{-1}(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}') + \phi(\mathbf{r}) v^{-1}(\mathbf{r} - \mathbf{r}') \phi(\mathbf{r}')] \right. \\ \left. + \lambda \int d\mathbf{r} h(\mathbf{r}) e^{v(0)/2 - i\phi(\mathbf{r})} \right\} \quad (37)$$

with the same definition for $h(\mathbf{r})$ as in eq.(5). As for the TCP, the Debye-Hückel propagator is defined by its inverse $v_{\text{DH}}(\mathbf{r}) = \ell_B e^{-\kappa r}/r$, but the screening length in this case reads $\kappa^2 = 4\pi\ell_B\lambda$. The partition function can be written as

$$Z_\lambda = e^{\lambda V + \lambda V v(0)/2} \frac{Z_{\text{DH}}}{Z_v} \left\langle e^{\lambda \int d\mathbf{r} Q(\mathbf{r})} \right\rangle \quad (38)$$

where

$$Q(\mathbf{r}) \equiv h(\mathbf{r})e^{v(0)/2 - i\phi(\mathbf{r})} - 1 - v(0)/2 + \phi^2(\mathbf{r})/2 \quad (39)$$

The logarithm of the partition function again follows by cumulant expansion,

$$\frac{\ln Z_\lambda}{V} = 2\lambda + \lambda v(0) + V^{-1} \ln \left[\frac{Z_{\text{DH}}}{Z_v} \right] + \lambda Z_1 + \frac{\lambda^2}{2} Z_2 + \dots \quad (40)$$

with Z_1 and Z_2 defined as in eqs.(9) and (10). The difference between the Debye-Hückel and the bare Coulomb self energy reads

$$\Delta v_0 = v(0) - v_{\text{DH}}(0) = 2\ell_B \sqrt{\pi\ell_B \lambda}, \quad (41)$$

the functions Z_1 and Z_2 are given by

$$Z_1 = e^{\Delta v_0/2} - 1 - \Delta v_0/2 \quad (42)$$

$$Z_2 = \int d\mathbf{r} \left[e^{\Delta v_0 - w(\mathbf{r}) - v_{\text{DH}}(\mathbf{r})} - e^{\Delta v_0} + \frac{1}{2} v_{\text{DH}}^2(\mathbf{r}) \left(1 - 2e^{\Delta v_0/2} \right) \right] \quad (43)$$

The DH contribution to the free energy follows as

$$\lambda v(0) + V^{-1} \ln \left[\frac{Z_{\text{DH}}}{Z_v} \right] = \frac{(4\pi\ell_B \lambda)^{3/2}}{12\pi} \quad (44)$$

Next we have to systematically carry out the back-Legendre transform to the canonical ensemble. To do this, we expand the grand-canonical potential in fractional powers of the rescaled fugacity,

$$\frac{a^3 \ln Z_\lambda}{V} = \tilde{\lambda} - b_{3/2} \tilde{\lambda}^{3/2} - b_2 \tilde{\lambda}^2 \dots \quad (45)$$

The rescaled concentration of ion pairs, $\tilde{c} = a^3 N/V$, is given by

$$\tilde{c} = \frac{\lambda a^3 \partial \ln Z_\lambda / V}{\partial \lambda}. \quad (46)$$

The fugacity as a function of the concentration is given by

$$\tilde{\lambda} = \tilde{c} + \frac{3}{2} b_{3/2} \tilde{c}^{3/2} + \left(2b_2 + \frac{27}{8} b_{3/2}^2 \right) \tilde{c}^2 \dots \quad (47)$$

The free energy density follows as

$$\begin{aligned} a^3 f &= -\frac{a^3 \ln Z_\lambda}{V} + \tilde{c} \ln \tilde{\lambda} \\ &= \tilde{c} \ln \tilde{c} - \tilde{c} + d_{3/2} \tilde{c}^{3/2} + d_2 \tilde{c}^2 + \dots \end{aligned} \quad (48)$$

The prefactors are given by

$$d_{3/2} = b_{3/2} = -\frac{2}{3} \sqrt{\pi} \epsilon^{3/2}, \quad (49)$$

$$d_2 = b_2 + \frac{9}{8} b_{3/2}^2. \quad (50)$$

The leading term of Z_2 is

$$Z_2 = -\bar{v} + \frac{2\pi a^3}{3} \left(\epsilon^3 \left[\gamma + \ln \epsilon + \Gamma(\epsilon) - \Gamma(3\sqrt{4\pi\epsilon\tilde{\lambda}}) - 11/6 \right] - e^{-\epsilon} [2 - \epsilon + \epsilon^2] \right) + \mathcal{O}(\tilde{\lambda}) \quad (51)$$

and the leading term of Z_1

$$Z_1 = \frac{\pi\epsilon^3\tilde{\lambda}}{2} + \mathcal{O}(\tilde{\lambda}^2). \quad (52)$$

The infinite constant $\bar{v} = \int d\mathbf{r} v(\mathbf{r})$ corresponds to the interaction of the ions with the oppositely charged background and the background self energy and will be neglected in the following. The quadratic coefficient of the free energy reads

$$d_2 = -\frac{\pi}{3} \left(\epsilon^3 \left[\gamma + \ln \epsilon + \Gamma(\epsilon) - \Gamma(3\sqrt{4\pi\epsilon\tilde{c}}) - 11/6 \right] - e^{-\epsilon} [2 - \epsilon + \epsilon^2] \right). \quad (53)$$

In Fig. 2a we plot this coefficient as a function of ϵ in the limit of small coupling strengths and setting $\tilde{c} = 1$ inside the logarithm. As one can see, in the zero-coupling limit, $\epsilon \rightarrow 0$, this coefficient becomes

$$d_2 = \frac{2\pi}{3}, \quad (54)$$

the standard second-virial result. We observe a non-monotonic behavior of the coefficient d_2 , and for $\epsilon > 3.5$ it becomes in fact negative.

For large values of ϵ , which corresponds to strong Coulomb interaction or relatively small hard-core diameter, the free energy density is conveniently rescaled by the Bjerrum volume ℓ_B^3 and reads

$$\ell_B^3 f = \hat{c} \ln \hat{c} + \hat{d}_{3/2} \hat{c}^{3/2} + \hat{d}_2 \hat{c}^2 + \dots \quad (55)$$

where we introduced the rescaled concentration $\hat{c} = \ell_B^3 c$ (which is related to the so-called plasma parameter Γ , which is commonly used to characterize a OCP, by $\Gamma^3 = 4\pi\hat{c}/3$). The coefficient appearing in this free energy expansion are

$$\hat{d}_{3/2} = -\frac{2}{3}\sqrt{\pi}, \quad (56)$$

$$\hat{d}_2 = -\frac{\pi}{3} \left(\gamma + \ln \epsilon + \Gamma(\epsilon) - \Gamma(3\sqrt{4\pi\hat{c}/\epsilon^2}) - 11/6 - \epsilon^{-3} e^{-\epsilon} [2 - \epsilon + \epsilon^2] \right). \quad (57)$$

In Fig. 2b we plot d_2 as a function of ϵ for large values of ϵ , again setting the concentration appearing inside the logarithm equal to unity. In the strong-coupling limit, $\epsilon \rightarrow \infty$, the coefficient approaches the value

$$\hat{d}_2 = -\frac{\pi}{3} \left[2\gamma - 11/6 + \ln(3\sqrt{4\pi\hat{c}}) \right], \quad (58)$$

which agrees exactly with the result obtained by Abe, by performing an infinite resummation of terms of the Mayer expansion [4]. His calculation was done without hard-cores, and thus constitutes a special case of our more general result for arbitrary hard-core diameter. In Fig. 2b we denote the Abe limit, $\hat{d}_2 = -\frac{\pi}{3} [2\gamma - 11/6 + \ln(3\sqrt{4\pi})] \simeq -1.76476$ by a broken line. As one can see, the convergence towards the asymptotic Abe result is quite slow, and even for strongly charged spheres with $\epsilon = 10$ the actual coefficient \hat{d}_2 has reached only one half of its asymptotic value.

IV. DISCUSSION

In this paper we introduce a novel field-theoretic formulation for plasmas and charged electrolyte or colloidal solutions. We are able to include, in addition to the Coulomb interactions, hard-core or excluded volume interactions. We apply our method to the one-component plasma (OCP) and the symmetric two-component plasma (TCP) and obtain, as a main result, the first few terms in a systematic low-density expansion of the free energy. The major advantage over previous calculational methods is that each order in the density expansion, which corresponds to an infinite Mayer sum, is reexpressed as a single diagram involving a composite, non-linear, but local operator. This entails that our results are non-perturbative with respect to the coupling strength $\epsilon = \ell_B/a$, and are thus valid both for vanishing electric charge, $\epsilon \rightarrow 0$, in which case we recover the virial expansion for a hard-core gas, and for vanishing hard-core diameter, $\epsilon \rightarrow \infty$. In the strong-coupling limit, $\epsilon \rightarrow \infty$, our results for the OCP asymptotically approach the previous results by Abe, but even for values of the coupling parameter as large as $\epsilon \simeq 10$ the differences to the asymptotic result are quite large. The TCP, on the other hand, does not have a well-defined strong-coupling

limit, and we find the expansion coefficients of the free energy to increase progressively as the coupling parameter increases. This fact is connected with the formation of strongly associated ion pairs. One of the motivations of the present work was to elucidate the critical behavior of the TCP, which shows a critical point at a coupling strength of roughly $\epsilon \simeq 15$. It is clear that unless resummation techniques of the low-density expansion are used, the low-density expansion cannot be used to predict the location of this critical point.

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FIG. 1. Plot of the coefficients d_2 and $d_{5/2}$ in a systematic and exact low-density expansion of the free energy for the symmetric two-component plasma (TCP). The coefficients are shown as a function of the coupling strength $\epsilon = \ell_B/a$, where $\ell_B = q^2/(4\pi\epsilon k_B T)$ is the distance at which two charged particles interact with thermal energy, and a is the hard-core diameter. It is seen that the coefficients diverge exponentially as ϵ increases.

FIG. 2. Plot of the quadratic free energy coefficient in the small-coupling limit, a), and in the strong coupling limit, b). For $\epsilon \rightarrow 0$, one recovers the hard-core virial coefficient, $d_2 = 2\pi/3$, and for $\epsilon \rightarrow \infty$ the Abe result is obtained, which is denoted by a broken line.

Fig. 1a, Netz and Orland

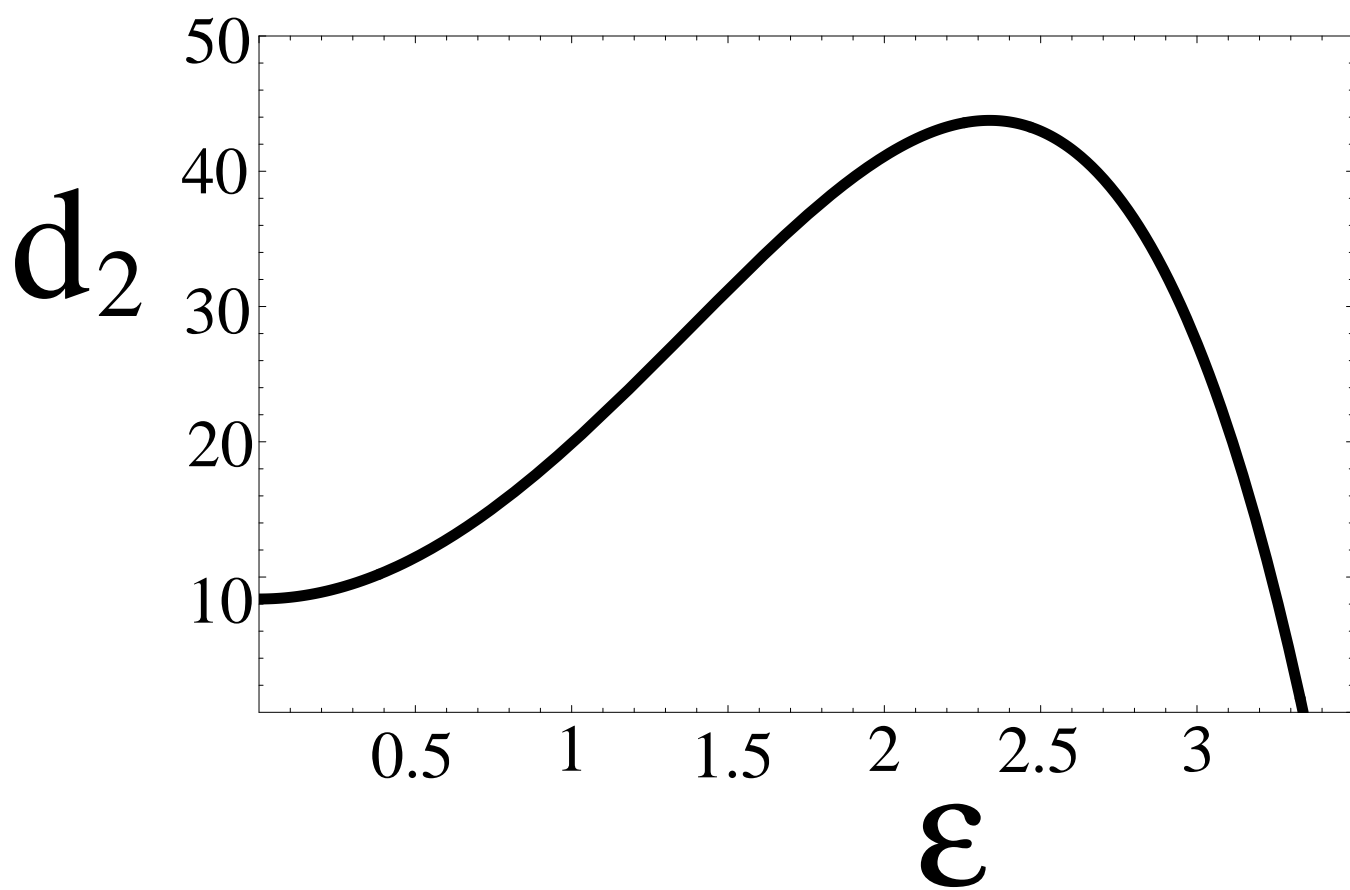


Fig. 1b, Netz and Orland

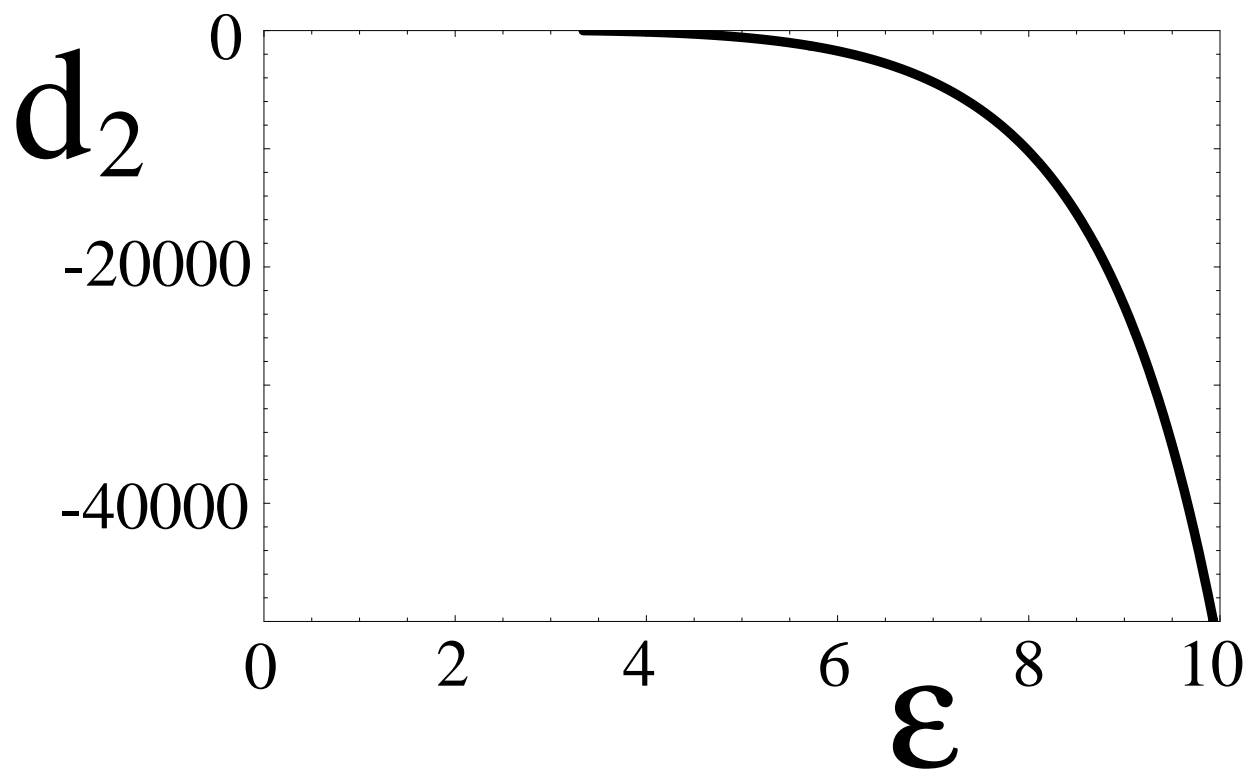


Fig. 1c, Netz and Orland

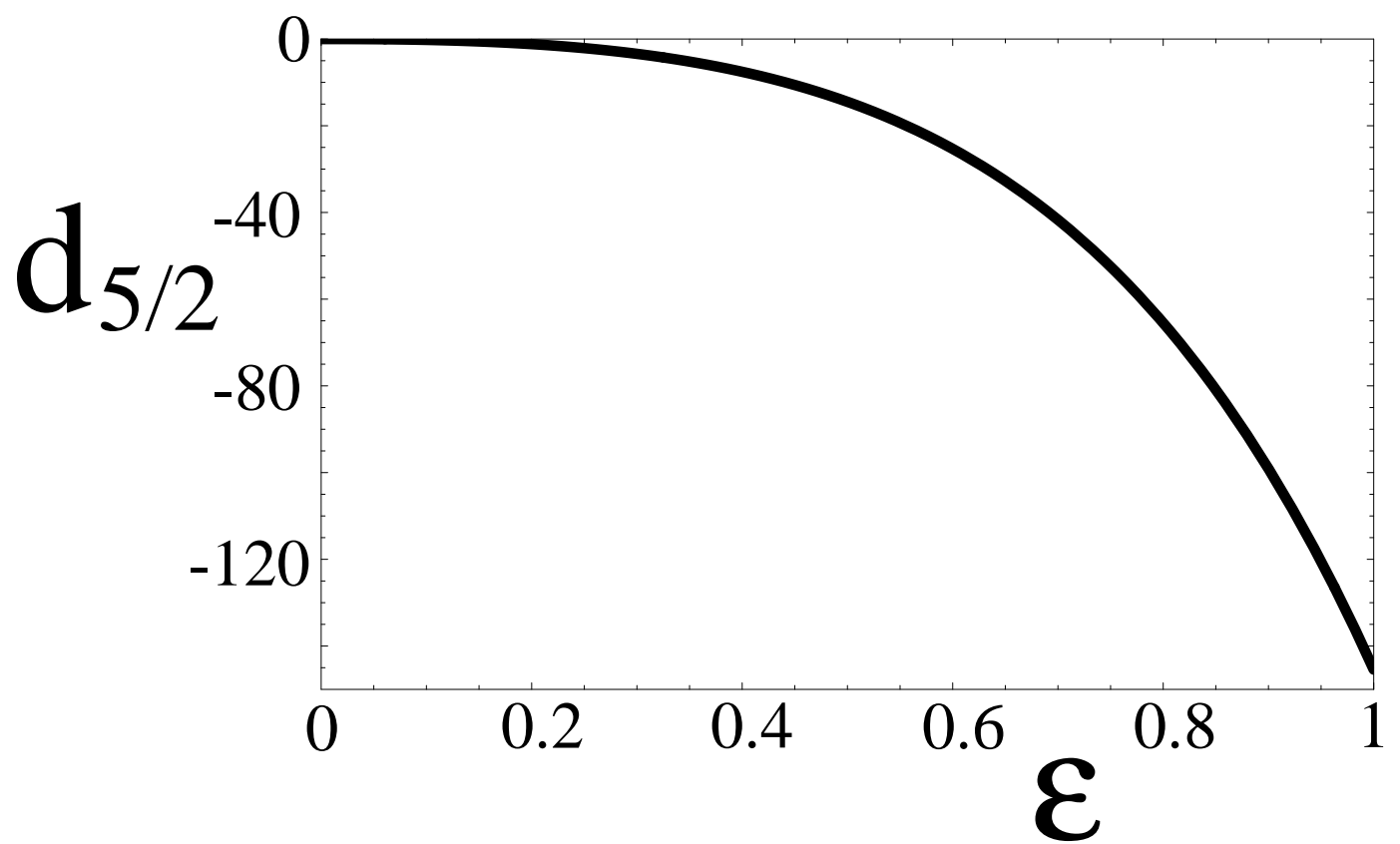


Fig. 1d, Netz and Orland

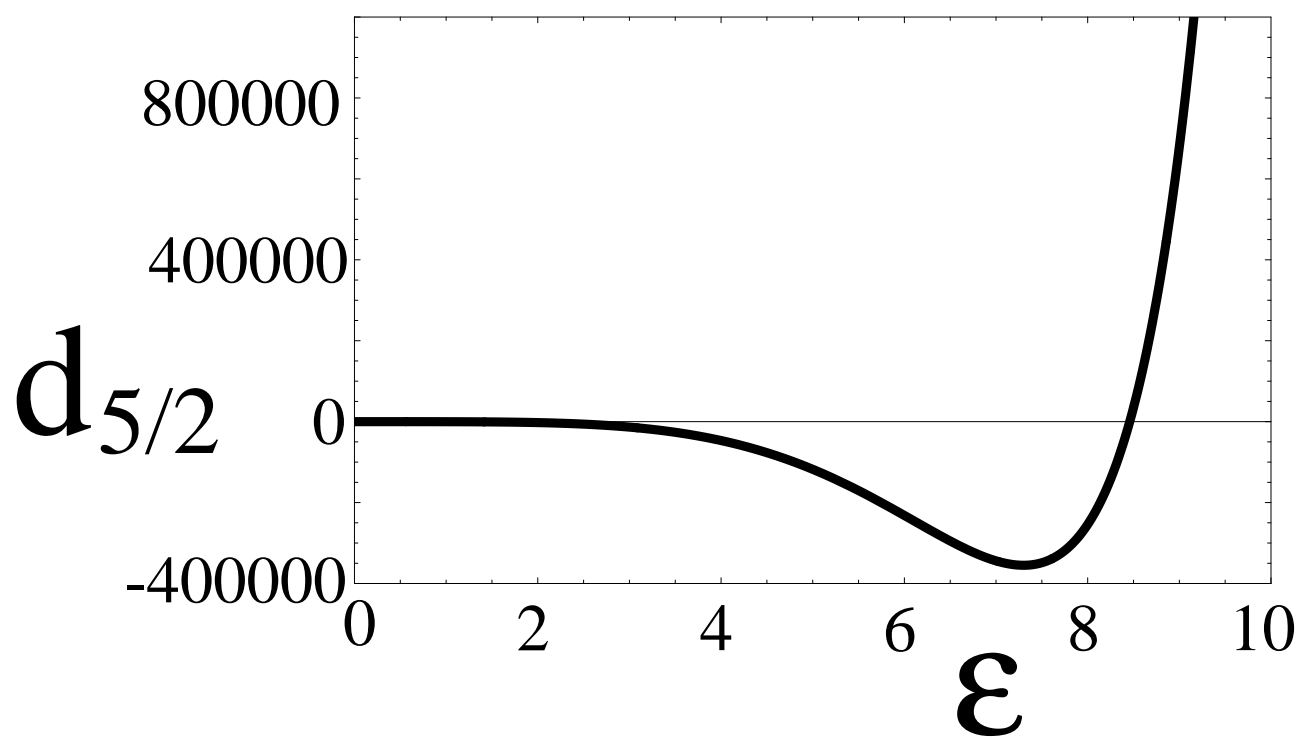


Fig. 2a, Netz and Orland

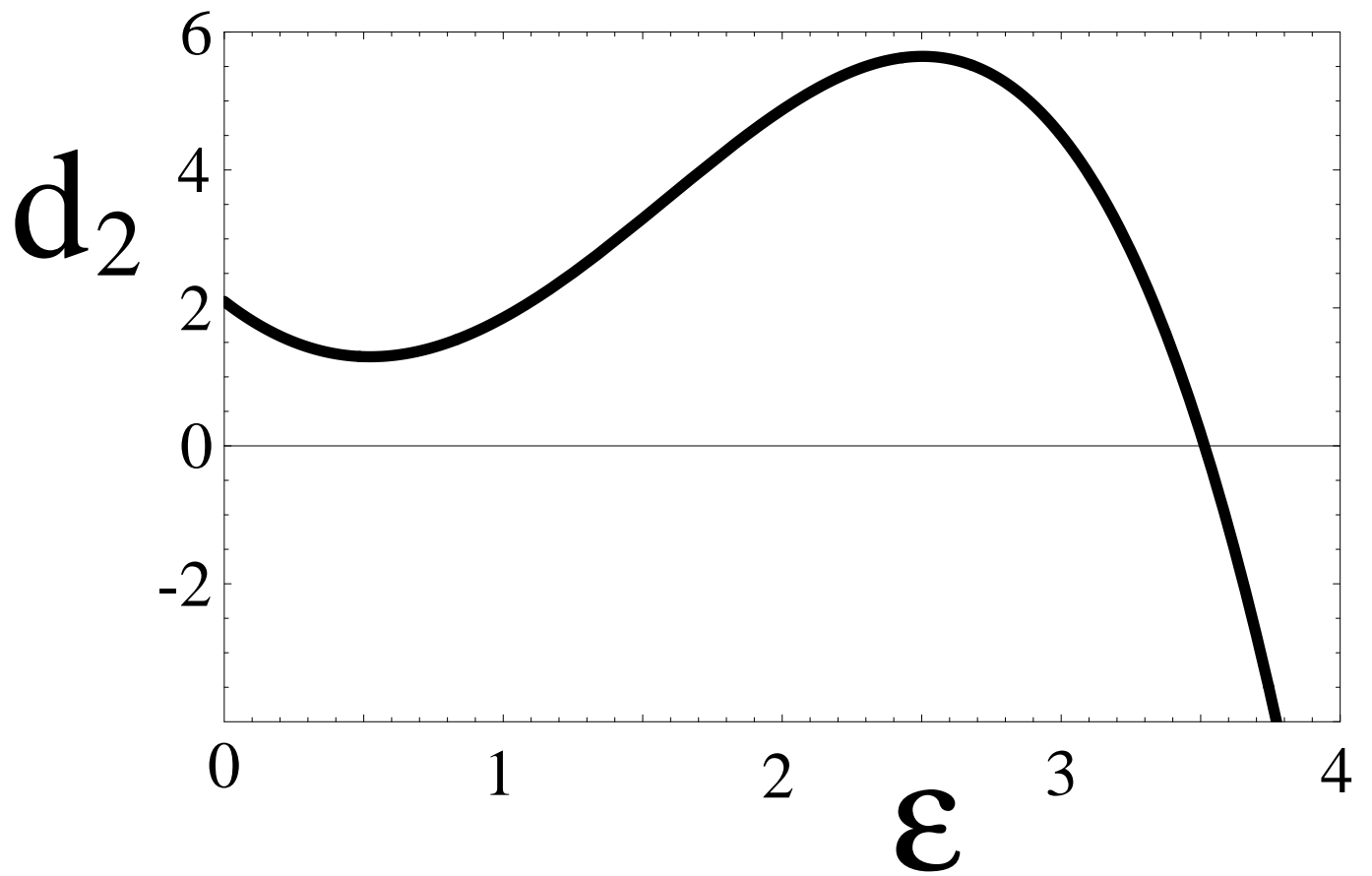


Fig. 2b, Netz and Orland

